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| 13. ABSTRACT (Maximum 200 words)<br><p>THE ARMY IS CONCERNED WITH THE REMOVAL OF DIMETHYLMETHYLPHOSPHONATE (DMMP) AND TRIMETHYLPHOSPHATE (TMP) FROM WATER BY TREATMENT WITH ACTIVATED CARBON. IN ORDER TO EFFECTIVELY EVALUATE THE REMOVAL OF THESE CONTAMINANTS FROM WATER, A RELIABLE METHOD IS REQUIRED TO MEASURE THE CONCENTRATION OF THESE CONTAMINANTS PRESENT IN THE WATER BEFORE AND AFTER TREATMENT. DETERMINATION OF THESE COMPOUNDS IN PREVIOUS CONTRACT WORK (DAAK11-78C-0132) USING THE EPA PRIORITY POLLUTANT PROTOCOL GAVE LOW AND ERRATIC RECOVERIES. THE PURPOSE OF THIS STUDY IS TO TEST AND EVALUATE AN ANALYTICAL METHOD, PROVIDED BY THE DEPARTMENT OF THE ARMY, FOR DMMP AND TMP IN AQUEOUS SOLUTION. THIS METHOD DIFFERS FROM THE EPA PRIORITY POLLUTANT PROTOCOL IN THAT A MACRORETICULAR RESIN, XAD-4, WILL BE USED TO EXTRACT DMMP AND TMP FROM AQUEOUS SOLUTION.</p> |   |  |   |                                  |
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Final Report

on

Evaluation of an XAD-4 Resin Extraction  
Method for Dimethylmethylphosphonate and  
Trimethylphosphate in Water

to

United States Army Armament Research and Development Command  
Edgewood Area, Aberdeen Proving Ground, Maryland  
from Calgon Analytical Laboratories, Pittsburgh, Pa. December 13, 1979

I. INTRODUCTION

The Army is concerned with the removal of dimethylmethylphosphonate (DMMP) and trimethylphosphate (TMP) from water by treatment with activated carbon. In order to effectively evaluate the removal of these contaminants from water, a reliable method is required to measure the concentration of these contaminants present in the water before and after treatment. Determination of these compounds in previous contract work (DAAK11-78C-0132) using the EPA priority pollutant protocol gave low and erratic recoveries.

II. OBJECTIVE

The purpose of this study is to test and evaluate an analytical method, provided by the Dept. of the Army, for DMMP and TMP in aqueous solution. This method differs from the EPA priority pollutant protocol in that a macroreticular resin, XAD-4, will be used to extract DMMP and TMP from aqueous solution.

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### III. EXPERIMENTAL

#### A. Preparation of XAD-4 Resin Columns

All of the Amberlite XAD-4 resin (Supelco, Inc., Bellefonte, Pa.) used in this study was cleaned prior to its use by Soxhlet extraction of 80 - 90 g aliquots of the resin for eight hours with three hundred ml of methanol (Burdick and Jackson, Inc., Muskegon, Mich.). Following extraction, the clean resin was transferred to a clean, covered one liter Erlenmeyer flask and stored under fresh methanol until its use.

The resin columns were prepared by wet packing a 250 ml Chromaflex column (Kontes Glass Co., Vineland, N.J.) with approximately 30 ml of the methanol extracted XAD-4 resin. Each resin column was then washed with 200 ml of methanol followed by 1000 ml of distilled water and maintained wet until introduction of the sample.

#### B. Sample Preparation

One liter solutions of DMMP and TMP containing 10, 20, 50, 100, 500, and 1000 ug/l of each compound in equal concentrations were prepared by serial dilution (Table I) in standard water as defined in Section IV C.3 of the Quality Assurance Program for the U. S. Army Toxic and Hazardous Materials Agency. Each spiked solution was then passed through a prepared XAD-4 column at a flow rate of approximately five ml per minute. The columns were subsequently eluted with two hundred ml of methanol, which was collected in a 250 ml Kuderna-Danish evaporative concentrator. The methanol extracts were concentrated to ten ml at 50°C under a gentle stream of air for subsequent analysis by FPD-GC.

Each concentration of the spiked samples was run twice a day on four separate, but not consecutive, days. Two blank (unspiked) samples were run each day that spiked samples were run.

#### C. Sample Analysis

Calibration standards containing 1 and 100 mg/l DMMP and TMP were prepared in methanol. The 1 mg/l calibration standard was prepared by serial dilution of the 100 mg/l standard.

All of the calibration standards, blank extracts, and spiked sample extracts were analyzed by FPD-GC using the instrumental operating conditions listed in Table II.

TABLE I

Preparation of DMMP and TMP Spiked Solutions

| <u>Volume of Stock<br/>Solution* (ml)</u> | <u>Final Volume of<br/>Spiked Sample (ml)</u> | <u>Nominal DMMP<br/>Conc. (ug/l)</u> | <u>Nominal TMP<br/>Conc. (ug/l)</u> |
|---|---|--------------------------------------|-------------------------------------|
| 0.1**                                     | 1000  | 11.0                                 | 10.3                                |
| 0.2**                                     | 1000  | 22.1                                 | 20.6                                |
| 0.5**                                     | 1000  | 55                                   | 51                                  |
| 1.0**                                     | 1000  | 110                                  | 103                                 |
| 5.0***                                    | 1000  | 552                                  | 514                                 |
| 10.0***                                   | 1000  | 1103                                 | 1028                                |

\*Stock solution composed of 110.3 mg/l DMMP + 102.8 mg/l TMP in distilled water.

\*\*Serial dilution made with an Eppendorf pipet.

\*\*\*Serial dilution made with a Mohr pipet.

TABLE II

GC Operating Conditions for DMMP and TMP Analyses

|                                  |  |             |
|----------------------------------|--|-------------|
| Instrument:                      | Perkin-Elmer Model 3920B GC equipped with flame photometric detector |             |
| Recorder:                        | Hewlett-Packard Model 3380A Recording Integrator                     |             |
| Column:                          | 6' x 2 mm I.D. glass packed with 80/100 mesh Chromosorb 101          |             |
| Column Temperature:              | 210°C  |             |
| Injector/Interface Temperatures: | 250°C  |             |
| Carrier Gas:                     | 50 ml/min. helium  |             |
| Sample Size:                     | 2 - 4 ul   |             |
| Retention Times:                 | Dimethylmethylphosphonate  | 5.3 minutes |
|                                  | Trimethylphosphate   | 6.0 minutes |

#### IV. RESULTS

All of the raw data generated by this study as well as the recovery and precision data obtained for DMMP and TMP using the method previously described, are presented in Tables III, IV, V, and VI. The recoveries of DMMP from water using this method ranged from 56 - 69% while the recoveries of TMP ranged from 61 - 86%. The relative standard deviation of the DMMP results for this procedure ranged from 25 - 73% (CL, 95%) while the RSD of the TMP results ranged from 30 - 80% (CL, 95%). The empirical detection limits for both DMMP and TMP were determined to be 3 ug/l. This figure is roughly consistent with the Hubaux - VOS<sup>1</sup> detection limits of 5.5 ug/l DMMP and 5.3 ug/l TMP.

#### V. DISCUSSION

While the recoveries for DMMP and TMP are generally acceptable, particularly at the lower concentrations of each, the precision of this method is generally poor. To a large extent, the poor repeatability of this method is due to the outgassing of air from the aqueous samples as they pass through the resin column. This leads to the formation of air pockets within the column which in turn shift the resin bed and lead to channelling. This problem is particularly acute when the methanol used to elute the column and residual sample left in the column mix.

In any event, the results obtained with this method represent a substantial improvement over the results obtained with the EPA priority pollutant protocol in the previous contract work. However, I believe that comparable recoveries with improved precision could be obtained with liquid-liquid extraction by "salting-out" the DMMP and TMP. This approach, if successful, could significantly reduce the amount of sample preparation time required for this analysis.

<sup>1</sup>Hubaux, A. and Vos, G., Analytical Chemistry 42, 849-885 (1970).







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TABLE V

Statistical Analysis of DMMP Recovery

| <u>Number of<br/>Observations</u> | <u>Nominal DMMP<br/>Conc. (ug/l)</u> | <u>Recovered DMMP Conc. (ug/l)</u> |               |                | <u>% Recovery<br/>Based on Mean<br/>Recovered<br/>Amount</u> | <u>RSD, %<br/>CL, 95%</u> |
|-----------------------------------|--------------------------------------|------------------------------------|---------------|----------------|--|---------------------------|
|                                   |                                      | <u>Mean</u>                        | <u>Range*</u> | <u>SD (2σ)</u> |  |                           |
| 8                                 | 11.0                                 | 6.8                                | 6.3           | 4.0            | 62   | 59                        |
| 8                                 | 22.1                                 | 13.1                               | 10.8          | 9.6            | 59   | 73                        |
| 8                                 | 55                                   | 35                                 | 25            | 20             | 64   | 55                        |
| 8                                 | 110                                  | 69                                 | 30            | 20             | 63   | 30                        |
| 8                                 | 552                                  | 381                                | 131           | 96             | 69   | 25                        |
| 8                                 | 1103                                 | 618                                | 399           | 254            | 56   | 41                        |
| 8                                 | Blank                                | 23                                 | ---           | ---            | ---  | ---                       |

\*Range = maximum value - minimum value

TABLE VI

Statistical Analysis of TMP Recovery

| <u>Number of<br/>Observations</u> | <u>Nominal TMP<br/>Conc. (ug/l)</u> | <u>Recovered<br/>Mean</u> | <u>TMP Conc. (ug/l)<br/>Range*</u> | <u>SD (2σ)</u> | <u>% Recovery<br/>Based on Mean<br/>Recovered<br/>Amount</u> | <u>RSD, %<br/>CL, 95%</u> |
|-----------------------------------|-------------------------------------|---------------------------|------------------------------------|----------------|--|---------------------------|
| 8                                 | 10.3                                | 6.3                       | 2.4                                | 2.2            | 61   | 34                        |
| 8                                 | 20.6                                | 17.7                      | 17.8                               | 14.2           | 86   | 80                        |
| 8                                 | 51                                  | 43                        | 28                                 | 26             | 84   | 60                        |
| 8                                 | 103                                 | 82                        | 39                                 | 24             | 80   | 30                        |
| 8                                 | 514                                 | 435                       | 206                                | 170            | 85   | 39                        |
| 8                                 | 1028                                | 740                       | 451                                | 340            | 72   | 46                        |
| 8                                 | Blank                               | < 3                       | ---                                | ---            | ---  | ---                       |

\*Range = maximum value - minimum value